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Gentlemen

Enclosed for your review and approval is the Operable Unit (OU) 5 Chemical Specific Matrix Effects Evaluation proposed for use in the Human Health Risk Assessment.

This evaluation addresses chemical specific matrix effects for chemicals of concern in soil and sediments

This discussion has been prepared in response to comments received on the OU 5 Exposure Assessment Technical Memorandum (EATM #12) and will be incorporated into the Remedial Investigation/Remedial Facility Investigation Report

If there are any questions regarding this request, please contact Kurt Muenchow at 966 2184

Sincerely

Steven W. Slaten  
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Enclosure

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## ATTACHMENT 1 CHEMICAL-SPECIFIC MATRIX EFFECTS

This attachment discusses the development of chemical specific matrix effects for Rocky Flats Environmental Technology Site (RFETS) Operable Unit No 5 (OUS) chemicals of concern (COCs) in soil and sediment samples. The attachment begins with its purpose and the OUS matrix effect. This is followed by a discussion of how the matrix effect was determined by describing chemical specific matrix factors for both inorganic and organic chemicals.

### Purpose

This attachment is a presentation of the chemical specific matrices for OUS COCs for which toxicity factors were derived from studies in which the agent was administered in solution. The matrix effect is used to account for decreased bioavailability relative to drinking water or other solutions such as corn oil where information on matrices are limited or do not exist.

As indicated in U.S. Environmental Protection Agency (EPA) guidance for risk assessment, adjustments of bioavailability may be necessary if the medium of exposure in the site exposure assessment differs from the medium of exposure assumed by the toxicity value (EPA 1989). The guidance further states that a substance might be more completely absorbed following exposure to contaminated drinking water than following exposure to contaminated food or soil (e.g., if the substance does not desorb from soil in the gastrointestinal tract). Although these matrix effect values were initially developed for the soil ingestion pathway, they also apply to other media where significant binding of compounds to a solid matrix may occur (e.g., compounds ingested from sediments or compounds ingested in homegrown produce).

### Derived Matrix Factor

For RFETS OUS COCs in soil and sediment whose toxicity factors were derived from studies in which the agent was administered in solution, a matrix factor of 0.5 was used to calculate intake for human health risk assessment (HHRA). Chemical specific matrix effects for OUS COCs in soil are listed in Table 1. The matrix effect of 0.5 is a conservative value derived from a review of literature summarized in Table 2. This value is based in part on:

EPA-derived relative bioavailability factors for cadmium in food (0.5) and lead in soil (0.6) (EPA 1995)

• 1 - ... derived relative bioavailability factor of 0.7 for soil (Fedorac et al 1990)

The evidence supports a 50 percent relative bioavailability of semivolatile organic compounds (SVOCs) in soil (Goor et al 1991 Ney 1990)

Note that several studies discussed in the section discussing the derivation of the chemical specific matrix effects indicate that the decrease in bioavailability from the matrix effects of food and soil can be substantially greater than 50 percent (as much as 99 percent) indicating that a matrix effect of 0.5 is conservative (Freeman et al 1992 Cox et al 1975 Sunagawa 1981 Heard and Chamberlain 1982 Sunderland et al 1989 EPA 1995)

Table 1 shows that the following OUS COCs in surface and subsurface soil or sediments had toxicity values which were derived from studies using drinking water or other solutions and therefore should be evaluated using a matrix effect of 0.5

Antimony  
Aroclor 1254  
Beryllium  
Fluoranthene  
Pyrene

Where the critical toxicity study was due and no vehicle was indicated in IRIS a default matrix effect of 1 will be used. This was the case for benzo(a)pyrene (BaP) and copa. On polycyclic aromatic hydrocarbon (PAH) COC for aquatic equivalence factors (TEFs) based on BaP [benzo(a)anthracene benzo(b)fluoranthene benzo(2,3-b)aceone and benzo(1,cd)pyrene] (EPA 1994a) we assigned a default matrix effect of 1 by analogy to BaP. For COCs where the chemical was injected directly into the ecosystem (e.g. SLIDE or one or more intravenous) it was not necessary to apply a matrix effect. This was the case for mercury and copper. Cadmium molybdenum and nickel were mixed directly into the diet and therefore a default matrix effect of 1 will be used.

For carcinogenesis studies factors were derived mostly from epidemiological studies (EPA 1994b). Slope factors calculations assume that each carcinogen is ingested in a soluble form in food or water and that it would therefore be absorbed orally or come via passive diffusion or in the case of the radionuclides is bound within a soil matrix. The absorption in intestinal intake and toxic effects cannot be quantified by multiplying the slope factor by a soil matrix effect because the

consider this account to reflect small effects of matrix on bioavailability of organics. The entire 2 matrix effect of 1 has been adopted for radionuclides in the present HRA even though this factor probably over estimates the effects of radionuclides ingested in soil and sediment.

### Derivation of the Chemical Specific Matrix Effect

The derivation of the O5 matrix effect was completed from the literature for several chemicals. Matrix effects for each of these chemicals are listed in Table 2 and the literature values for matrix effects shown in Table 2 are discussed in the following paragraphs organized by inorganic and organic chemicals. Various studies are cited (some that used OUS COCs and some that did not) that provide the rationale to use the matrix effects that are identified in Table 1.

#### Inorganic Chemicals

Six examples of EPA precedence for assuming decreased bioavailability of inorganics from food and soil compared to that in water are presented in the following discussion. Following these paragraphs are examples of decreased bioavailability of inorganics in soil versus solution from the available toxicological literature.

Cadmium (an OUS COC) and manganese (not a COC in soil or sediment) each have two EPA derived oral reference doses (RfDs) one for ingestion in food and one for ingestion in water. In deriving media specific RfDs for cadmium, EPA assumed that 5 percent of cadmium ingested in water is bioavailable ( $RfD = 1.0E-0$  mg/kg-d) compared to 10-5 percent of cadmium ingested in food ( $RfD = 1.0E-0$  mg/kg-d) (EPA 1995). Cadmium has an oral RfD for ingestion from food ingestion as seen in Table 1. Therefore there is no need for a matrix effect for cadmium and the default matrix effect of 1 was used for cadmium.

The RfD for manganese ingested in water ( $5.0E-0$  mg/kg-d) is 28 times less than the RfD for manganese ingested in food ( $1.4E-0$  mg/kg-d) (EPA 1995). Although relative bioavailability of manganese in food and water is not discussed in the Interated Risk Information System (IRIS), one explanation for a 28 fold decrease in toxicity of manganese ingested in food is a matrix effect resulting in greatly decreased bioavailability.

Another example of media specific differences in toxicity of inorganics is suggested by EPA's RfD for cyanide. In deriving the RfD for cyanide based on a dietary study in rats, EPA included a safety factor of 10 protecting for extrapolation in assessing toxicity of cyanide ingested in

<sup>a</sup> Legg et al. "Assumptions and Calculations for

use EPA 100%) to use 0.1 as for a compound which represents 0.001 COC times as toxic as cyanide ingested in water corresponding to a matrix effect of 0.2. This matrix effect is less than the conservative 0.5 matrix effect used for those chemicals whose toxicity values were derived from studies in which the agent was administered in solution (Table 1).

EPA does not discuss the matrix effect of beryllium (an OUS COC) in IRIS (EPA 1995). The IRIS file however presents an unpublished investigation by Cox et al (1975) which indicates a much higher no-observed-effect level (NOEL) of 25 mg/kg-d in the deer than that in the rat drinking water study used to derive the RfD of 5.0E-03 mg/kg-d (NOEL of 0.54 mg/kg bw/day) (Schroeder and Mutchner 1975). The corresponding matrix effect for beryllium is 0.02. This matrix effect is much less than the conservative 0.5 matrix effect used for those chemicals whose toxicity values were derived from studies in which the agent was administered in solution (Table 1).

Antimony another OUS COC has a RfD of 4.0E-04 mg/kg-d that was derived using a lowest observed adverse-effect level (LOAEL) of 0.55 mg/kg bw day from a chronic drinking water study with rats (Schroeder et al 1970). A LOAEL of 500 mg/kg was reported for rats fed me allic antimony for 24 weeks (Sunagawa 1981). The resulting matrix effect for antimony is 0.0007. This matrix effect is much smaller than the conservative 0.5 matrix effect used for those chemicals whose toxicity values were derived from studies in which the agent was administered in solution (Table 1).

EPA's Integrated Exposure-Lead Bioavailability Model (IEL-BM) for lead in water assumes that the bioavailability for lead ingested in soil is 50 percent compared to 50 percent bioavailability for lead ingested in water. The corresponding soil matrix value is 0.6 (EPA 100%).

Evidence in the available toxicological literature indicates that absolute absorption of inorganics ingested in food is less than that from water. Sixty percent of radiolabeled lead chloride administered to adult humans in water was bioavailable compared to 3 percent for lead chloride ingested in food (Heller and Chamberlain 1982). Similarly nickel chloride administered to adults in water was much less bioavailable (0.7 percent) than nickel chloride administered in food (28 percent) (Suzuki and et al 1989). Increased blood levels of manganese were observed in humans ingesting high doses in water. When similar doses of manganese were ingested with food (Baines et al 1987) blood levels of manganese were no increased.

available to toxicants in soil is less than in water. This is expected because iron limits only 50 percent of lead acetate in soil. Iron bioavailability of lead acetate ingested in soil was 8 percent of that of lead acetate injected in water (Freeman et al 1992). A arsenic administered in soil to rabbits was much less bioavailable (28 percent) than arsenic administered in water to rabbits (59 percent) corresponding to a soil matrix of 0.47 (Freeman et al 1993).

### Organic Chemicals

Several studies show that organic chemicals including pesticides also bind tightly to soil reducing their bioavailability through both oral and dermal exposure. Clays and organic colloids have a large surface area and cation exchange capacity which permits significant adsorption of virtually all classes of pesticides. Furthermore the adsorbed fraction desorbs slowly and is effectively a bound fraction that increases over time as the soil pesticide bond ages (Calderbank 1989). The bound fraction is estimated to be about 20 to 70 percent of the total amount of organic chemical applied to the soil.

McConnell et al (1984) showed using soil containing 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) from the Minkler Sludge site that 5 µg/kg bw TCDD in corn oil resulted in the death of all six treated guinea pigs and 13 ppm TCDD was detected in the animals' livers. In the same study 5 µg/kg bw TCDD from soil caused oral deaths of 6 treated animals with 1-4 ppm detected in the liver. This study indicates about 10 percent relative bioavailability of TCDD from the soil. Shue et al (1988) conducted further studies on TCDD and found an average of 14 percent (range of 25 to >0 percent) bioavailability of TCDD in rats receiving doses from Times Beach, Missouri.

Gonne et al (1991) showed that BaP aged 6 months in soil was only 3-10% percent orally bioavailable for clayey and sandy soils compared to BaP administered alone to rats. Polychlorinated biphenyls (PCBs) and pesticides like dichlorodiphenyltrichloroethane (DDT) chloro diane and heptachlor may be expected to adsorb strongly to soil similarly to BaP (Neu 1990). Thus PCB and pesticide adsorption onto eroded soils in reduced bioavailability due to this matrix effect. These studies support a conservative estimate of 50 percent relative bioavailability of SVOCs in soil compared to those in solution.

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**Table 1**  
**RFLTS OUS Soil Matrix Effects**

Chemical of Concern	Type of Critical Study			Matrix Effect <sup>b</sup>
	Oral Reference Dose	Oral Slope Factor	Vehicle	
Antimony	Drinking water (rats)	0.5	-	0.5
Aroclor 1254	Glycerol and corn oil vehicle (monkeys)	By analogy to Aroclor 1260 (corn oil vehicle stirred in food rats)	-	0.5
Benz(a)anthracene	-	-	-	-
Benzo(a)pyrene	-	-	-	-
Benzo(b)fluoranthene	-	-	-	-
Beryllium	Drinking water (rats)	0.5	Drinking water (rats)	0.5
Cadmium	Dietary (humans)	-	-	1
Cu(II) per	Oral dose vehicle not specified (humans)	-	-	1
Dibenz(a,h)anthracene	-	-	-	-
Fluoranthene	Gavage (mice)	0.5	Gavage (mice)	0.5
Indeno(1,2,3-cd)pyrene	-	-	-	-
Mercury	Intraparenchymal I.I.g(I, (rats)	N/A	-	N/A
Molybdenum	Dietary (humans)	1	-	1
Nickel	Dietary (rats)	1	-	1
Pyrrolidine	Gavage (mice)	0.5	Gavage (mice)	0.5
Silver	Intraventral injection (humans)	N/A	-	N/A

<sup>a</sup> See R2276 section d.4.a.i (v)

Table 1 (continued)

Chemical of Concern	Oral Reference Dose	Oral Slope Factor	Type of Critical Study	Matrix Effect <sup>b</sup>
Americium 241			Epidemiological studies (humans)	1
Plutonium 239/240			Epidemiological studies (humans)	1
Uranium 233/234			Epidemiological studies (humans)	1
Uranium 235			Epidemiological studies (humans)	1
Uranium 238			Epidemiological studies (humans)	1

N/A Not applicable chemical was administered directly into the receptor via injection

<sup>a</sup> Source ICRIS unless otherwise noted

<sup>b</sup> A soil matrix effect of 0.5 is reported by literature for COCs with toxicity values based on solution vehicles All other soil matrices are 1 See text and Table 2

c Adopted for all carcinogenic PAs in soil

**Table 2**  
**Derivation of RFETS OUT 0.5 Soil Matrix Effect**

Chemical/Species	Fraction Absorbed from Food/Soil (Fm)	Fraction Absorbed from Water (Fw)	Matrix Effect	Source
Caesium (human adults)	0.025	0.05	0.50 <sup>a</sup>	EPA (1995)
Manganese (human adults)	NA	NA	0.04	EPA (1995)
Cyanide (rats)	NA	NA	0.20 <sup>b</sup>	EPA (1995)
Beryllium (rats)	NA	NA	0.02 <sup>c</sup>	EPA (1995)
Antimony (rats)	NA	NA	0.0007 <sup>d</sup>	EPA (1995)
Lead (human adults)	0.03	0.6	0.05	Heard and Chamberlain (1982)
Nickel (human adults)	0.007	0.28	0.03	Sunderland et al (1989)
Lead (human children)	0.3	0.5	0.60 <sup>e</sup>	EPA (1994)
Lead (rats)	NA	NA	0.08 - 0.20 <sup>f</sup>	Freeman et al (1992)
Arsenic (rabbits)	0.28	0.59	0.47 <sup>g</sup>	Freeman et al (1995)
TCDD (guinea pigs)	NA	NA	0.10 <sup>h</sup>	McConnell et al (1984)
Benzo(a)pyrene (rats)	NA	NA	0.34 - 0.51	Goon et al (1991)

NA Not available from the data.

<sup>a</sup> Based on Fm/Fw

<sup>b</sup> Based on relative toxicity of manganese in water vs food (RD in water = 5.0E-03 mg/kg-d RD in food = 1.4E-01 mg/kg-d ratio = 0.04)

<sup>c</sup> Based on expected increase in toxicity of cyanide ingested in water

<sup>d</sup> Based on relative toxicity of beryllium in water vs food (NOEL in water = 0.54 mg/kg bw/day NOEL in food = 25 mg/kg-d)

<sup>e</sup> Based on relative toxicity of antimony in water vs food (LOAEL in water = 0.53 mg/kg bw/day LOAEL in food = 500 mg/kg-d)

<sup>f</sup> Based on relative retention of lead in blood, bone and liver from EPA's IEUBK lead model

<sup>g</sup> Based on relative retention of TCDD in the liver

<sup>h</sup> Based on relative bioavailability of benzo(a)pyrene from soil compared to water